IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of
Kazumi Naito
Serial No. 10/043,102
Filed: January 14, 2002

Group Art Unit: 1742
Primary Examiner:
Ngoclan T. Mai

For: NIOBIUM POWDER, SINTERED BODY THEREOF AND CAPACITOR USING THE SAME

DECLARATION UNDER 37 C.F.R. §1.132

Honorable Commissioner for Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Kazumi Naito, of c/o Central Research Laboratory, Showa Denko Kabushiki Kaisha, 1-1, Ohnodai 1-chome, Midori-ku, Chiba-shi, Chiba, 267-0056 Japan, being duly sworn, declare and state:

THAT I was awarded a bachelor's degree from the Department of Polymer Science, Faculty of Science, Osaka University in 1974, and a master's degree from the Faculty of Science, postgraduate course of the same university in 1976.

THAT I have been employed by Showa Denko Kabushiki Kaisha since 1976 where I was engaged on research and development of polymers from 1976 to 1981 and have been engaged on research and development of new capacitors since 1981;

THAT I am the sole inventor of the invention disclosed in th above-identified U.S. patent application, and henc I am fully familiar therewith;

THAT I was intimately involved with the preparation of the above-identified U.S. patent application, and that all th examples and comparative examples in the above-identified U.S. patent application correspond exactly to experiments made for preparing the application and by my knowledge are true; and that all statements made in association therewith in the above-identified U.S. patent application are made on information and belief and are believed to be true;

THAT, in order to show that a niobium powder containing cobalt or silicon in an amount of more than 100 ppm by weight gives a niobium sintered body exhibiting a large specific leakage current index and a capacitor exhibiting a large leakage current value, as compared with those which are made from a niobium powder containing cobalt or silicon in an amount of not more than 100 ppm by weight, the following comparative experiments were carried out by me or under my supervision as described below.

COMPARATIVE EXPERIMENTS

Experiment 1 (Present Invention)

By the same procedures as described in Example 9 in the specification of the above-identified U.S. patent application, a niobium sintered body was made and its characteristics were evaluated as follows.

A niobium rod (20 mmϕ, 20 g) was placed in a reactor made of SUS 304. After the reactor was degassed to attain vacuum (approximately 6×10^{-4} Torr), the temperature of the reactor was elevated to 800°C, and hydrogen was fed into the reactor. Hydrogen was further introduced at 350°C for 50 hours. After cooling, a hydrogenated niobium ingot was pulverized for 10 hours in a one-liter pot made of SUS 304 and containing iron balls. The pulverized product was placed into the above-described r actor made of SUS 304, and hydrogenated und r the sam conditions as mentioned abov . The thus-formed hydrog nated product was mixed with water, to prepare a 20 vol.% slurry, which

was pulv rized with zirconia balls by a wet-crusher made of SUS 304 (trade name, Attriter). The pulverizing time was 3 hours. The thus-obtained niobium powder had a mean particle diameter of 1.1 μm.

The niobium powder was sequentially washed with 95% sulfuric acid, water, a mixture of 30% hydrofluoric acid and 50% nitric acid (1 : 1 by weight), and water, and then dried in vacuum, to thereby remove impurities introduced during pulverization.

The amount of elements contained as impurities in the thus-obtained niobium powder was measured by the atomic absorption spectrometry. The results are shown in Table I.

The niobium powder was allowed to stand in a vessel filled with nitrogen for two hours at a temperature of 400°C to thereby induce nitridation. The nitrided niobium powder had a nitrogen content of 5,800 ppm by weight.

Subsequently, the nitrided niobium powder was shaped together with a niobium wire (0.3 mmϕ) into a compact having approximate dimensions of 0.3 cm x 0.18 cm x 0.45 cm (approximately 0.1 g). The compact was allowed to stand in vacuum of 3×10^{-5} Torr at 1,300°C for 30 minutes, to thereby produce a sintered body thereof. The sintered body was electrochemically converted through application of 20 V in a 0.1% aqueous solution of phosphoric acid at 80°C for 200 minutes, to thereby form a niobium oxide dielectric layer on a surface of the sintered body. Thereafter, the specific leakage current index was measured after application of voltage at 14 V for three minutes at room temperature in a 20% aqueous solution of phosphoric acid. The result is shown in Table II.

By the same procedures as described in Example 15 in the specification of the above-identified U.S. patent application, a chip capacitor was mad fr m the niobium sintered body, and characteristics of the capacitor were valuated as follows.

The sint red body was electrochemically converted at 20

V in a 0.1% aqueous solution of phosphoric acid for 200 minutes, to thereby form a dielectric niobium oxide film on the surface of the sintered body. Subsequently, the thus-treated sintered body was immersed in a mixture of a 35% aqueous solution of lead acetate and a 35% aqueous solution of ammonium persulfate (1 : 1 by volume) and heated at 40°C for one hour. This immersion-heating procedure was repeated, to thereby form on the dielectric niobium oxide film a layer comprising a lead dioxide-lead sulfate mixture (lead dioxide content of 94 wt.%), serving as the other electrode. A carbon layer and a silver paste layer were successively formed on the lead dioxide-lead sulfate mixture layer. A lead frame was placed on the thus-produced element, and the entirety thereof was encapsulated with an epoxy resin, to thereby produce a chip capacitor.

Leakage current value and capacitance of capacitor (average value of 50 capacitors) are shown in Table II. The leakage current value was measured after 6.3 V was imposed for one minute at room temperature.

Experiment 2 (Comparative Example)

A metallic cobalt powder having an average particle diameter of 0.2 μm was added to the same niobium powder as that prepared in Experiment 1 (which was subjected to the impurities-removing treatment but not yet subjected to nitridation in Experiment 1). The thus-obtained niobium powder contained elements as impurities in amounts shown in Table I.

By the same procedures as described in Experiment 1, the niobium powder was nitrided, and a niobium sintered body and a chip capacitor were made and their characteristics were evaluated. The results are shown in Table II.

Experiment 3 (Comparative Example)

A silicon powder (simple substance) having an average particl diamet r of 0.35 μm was added to the same niobium powder as that prepared in Experiment 1 (which was subjected to the impurities-removing treatment but not y t subjected to

nitridation in Experiment 1). The thus-obtained niobium powder contained lements as impurities in amounts shown in Table I.

By the same procedures as described in Experiment 1, the niobium powder was nitrided, and a niobium sintered body and a chip capacitor were made and their characteristics were evaluated. The results are shown in Table II.

Table I

	Content of impurity element [wt. ppm]							
	Fe	Ni	Co	Si	Na	K	Mg	Total
Experiment 1	20	20	20	30	5	5	5	105
Experiment 2	20	20	125	30	5	5	5	210
Experiment 3	20	20	20	165	5	5	5	240

Table II

	Sintered body	Capacitor chip	
	Specific LC index [pA/(μF·V)]	LC [μA]	Capacitance [μF]
Experiment 1	220	1.6	411
Experiment 2	760	16.4	423
Experiment 3	650	14.8	435

It will be seen from Experiments 2 and 3 (Comparative Examples) that, in the case when a niobium powder used contains a cobalt or silicon impurity in an amount exceeding 100 ppm by weight, a sintered body made from the niobium powder has an undesirably large specific leakage current index, and a capacitor made from the sintered body has an undesirably large leakage current.

In contrast, in the case when a niobium powder used contains each of the metal elements, including cobalt and silicon, specified in claim 1 of the above-identified U.S. patent application in an amount of not more than 100 ppm by weight (Experiment 1; Present Invention), a sintered body made from the niobium powder has a small specific leakage current index, and a capacitor made from the sintered body has a small leakage current.

I, the undersigned declarant, declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and; further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18, of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This twenty-fifth day of June, 2003

Kazumi Naito

Kazumi Naito